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Reductive Activation of *tripod* Metal Compounds: Identification of Intermediates and Preparative Application

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In memoriam Professor Dr. Ernst Otto Fischer

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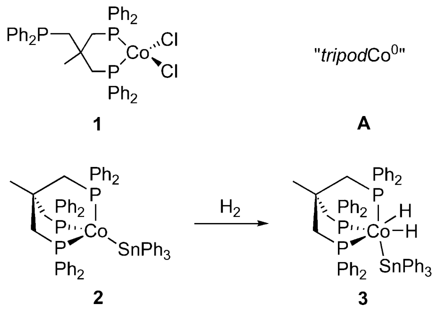
[*tripod*$CoCl_2$] {*tripod* = $CH_3C(CH_2PPh_2)_3$} when treated with KC_8 in THF solution under an argon atmosphere produces a reactive species ["*tripod*Co^0"] (**A**) which undergoes oxidative additions with stannanes, [*tripod*$Co(H)_2(SnBu_3)$] (**4**), formed, for example, by addition of Bu_3SnH. Silanes, R_3SiH, undergo the same type of reaction producing [*tripod*$Co(H)_2(SiR_3)$] (R = Et: **5a**; R = Ph: **5b**). The solid-state structures of all the compounds [*tripod*$Co(H)_2(ER_3)$] (E = Si, R = Ph; E = Sn, R = Ph, Bu) are rather similar. While they contain six-coordinate cobalt with the formal oxidation state of cobalt being +III the coordination geometry is not octahedral: the heteroelement E deviates from the position which it would have in octahedral coordination by around 40° while the other five ligands, three phosphorus and two hydrogen, have the expected interligand angles of around 90° and 180°, respectively. The deviation of the heteroelement E is such that it approaches the metal bonded hydrogen atoms leading to short H···E contacts of only about 190 pm (E = Si) and 230 pm (E = Sn), respectively. The generation of a reactive species ["*tripod*Co^0"] (**A**) was transferred to the synthesis of a reactive *tripod*nickel(0) species by treating a THF solution of [$(DME)NiBr_2$] with KC_8 in the presence of *tripod*. This species reacts with two electron donor ligands L to produce the pseudo tetrahedral compounds [*tripod*Ni(L)] {L = PPh_3 (**6**), $AsPh_3$ (**7**), cHexNC (**8**), *t*BuNC (**9**), C_2H_4 (**10**)}. The identity of the reactive nickel(0) species as unequivocally deduced from NMR experiments is [*tripod*$_4Ni_3$] (**12**). All compounds were characterised by the usual analytic techniques including X-ray analysis where applicable.

Introduction

The tripodal ligand [$CH_3C(CH_2PPh_2)_3$], henceforth called *tripod*, has a peculiar coordination chemistry: *tripod* metal templates have been shown to engage in coordination of rather unconventional coligands.[1] In many cases reductive activation of *tripod* metal precursors in the oxidation state +II, either as in the preparation of [*tripod*$Co(N_2)Co$*tripod*] by reduction of [$CoCl_2$] with Na/Hg in the presence of *tripod* under N_2 atmosphere,[2] or in the synthesis of [*tripod*$Co(\eta^3\text{-}P_3)$] from [$Co(BF_4)_2\cdot 6H_2O$], *tripod* and P_4,[3] is a key step in the synthesis.

It has been reported that reduction of a solution of [*tripod*$CoCl_2$] (**1**)[4] (Scheme 1) in THF by potassium graphitate, KC_8, in an atmosphere of argon leads to a compound which behaves as expected for the species ["*tripod*Co^0"] (**A**): with $HSnPh_3$ it reacts to produce [*tripod*$Co(SnPh_3)$] (**2**), which, under an atmosphere of H_2 yields the cobalt(III) species [*tripod*$Co(H)_2(SnPh_3)$] (**3**).[5] If $HSnBu_3$ is used instead of $HSnPh_3$, [*tripod*$Co(H)_2(SnBu_3)$] (**4**), an analogue of **3**, is immediately obtained.[5]



Scheme 1.

The aim of the work reported here was to further investigate the reactivity of the species presumed to be ["*tripod*Co^0"] (**A**) and, if possible, to elucidate its constitution.

Results and Discussion

THF solutions of the species described as ["*tripod*Co^0"] (**A**) were prepared as reported.[5] From these solutions [*tripod*$Co(H)_2(SnBu_3)$] (**4**) was obtained following the published procedures (Scheme 2).[5]

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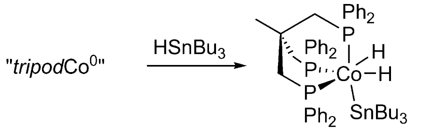
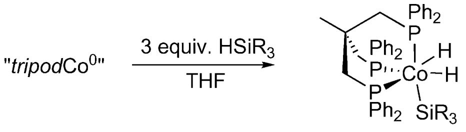


A **4**

Scheme 2.

4 had been fully characterised by standard analytical techniques.[5] The solid-state structure of **4**[6] referred to in this work (Table 1) was found to be analogous to that of **3** in all comparable details.

Freshly prepared solutions of **A** were found to react as well with silanes of the type $HSiR_3$. $HSiEt_3$, when added to a THF solution of **A**, produces [*tripod*$Co(H)_2(SiEt_3)$] (**5a**) (Scheme 3).



A **5a, b**

a: R = Et
b: R = Ph

Scheme 3.

While it was not possible to grow crystals of **5a**, its identity was unambiguously inferred from its mass spectrum and its ^1H and ^{31}P signature (see Exp. Sect.).

The compound [*tripod*$Co(H)_2(SiPh_3)$] (**5b**), as a silicon analogue of **3**, is obtained if the solution **A** is treated with $HSiPh_3$ (Scheme 3). **5b** has been characterised by the traditional analytic techniques including X-ray analysis (Table 1, Figure 1). It crystallises in the same orthorhombic space group $Pna2_1$ as **3**.[5] The cell dimensions (**5b**: a = 1857 pm, b = 1349 pm, c = 1900 pm) and volume ($V = 4759 \times 10^6$ pm^3) reflect the smaller radius of silicon as compared to tin (**3**: a = 1919 pm, b = 1355 pm, c = 1905 pm; $V = 4959 \times 10^6$ pm^3).[5] Distances and angles (not implying silicon and tin) are almost identical in **3**[5] and **5b**. The Co–Si distance in **5b** is 227.8(1) pm. The Co–Sn distance in **3** amounts to 249.4(1) pm.[5] The difference in length being well in accord with the difference of the covalent radii of the elements.[7] The position of the heteroatom E with respect to the *tripod*cobalt entity is again similar for both compounds **3** and **5b** (Table 1; cf. angles P1–Co–E: 134.8°/139.8°, P2–Co–E: 114.4°/110.8°, P3–Co–E: 118.5°/114.5° for **5b**/**3**). The Co–H distances are 134(3) pm and 132(3) pm in **5b** and 137(4) pm and 135(4) pm in **3**.[5] As a cobalt(III) compound, **5b** is expected to show octahedral coordination. The octahedron is, however, quite distorted (Figure 1, Table 1) as has also been found for **3**.[5] The distortion is such that the Si–H distances are only around 190 pm (Table 1) and thus only about 40 pm longer than a regular Si–H single bond. Similarly short non-bonded contacts between hydrogen and tin have been reported for **3**.[5] In this case coupling between the hydrogen nuclei and the tin nucleus as observed by NMR experiments[5] has been taken as additional evidence for a kind of agostic interaction. Even lacking this evidence for **5b** the short Si–H distances are in favour of this hypothesis. The ^1H resonances of the metal bonded hydrogen atoms appear as broad signals at δ = –13.45 (**5a**) and δ = –13.10 (**5b**) The IR spectrum of **5b** shows two Co–H vibrations at 1928 cm^{-1} and 1916 cm^{-1}. The two bands are of equal intensity as expected for the symmetric and asymmetric Co–H vibrations if the Co–H bonds are at 90° to each other.[8] By X-ray analysis this angle is found to be 87(2)°. The analytical data in a whole (see Exp. Sect.) are in full agreement with the constitutions and structures described.

The synthesis of **5b** was in so far of special importance as the yield of **5b** was found to be above 60% in analytically pure crystalline form. For the reactions reported so far the isolated yields had generally been quite a bit below 40% such that it could have been hypothesised that their formation might be due to the presence of some minor component present in solution **A**. This hypothesis is definitely ruled out by the high yield with which compound **5b** is obtained.

The experiments reported so far demonstrate that solutions **A** contain a coordinatively unsaturated species, but they shed no further light on the very nature of this species. All attempts to grow crystals of one of the species present in solution **A** and thus to elucidate their composition by X-ray analysis did not meet with success. Although FAB$^+$ mass spectrometric analysis of **A** shows strong signals for

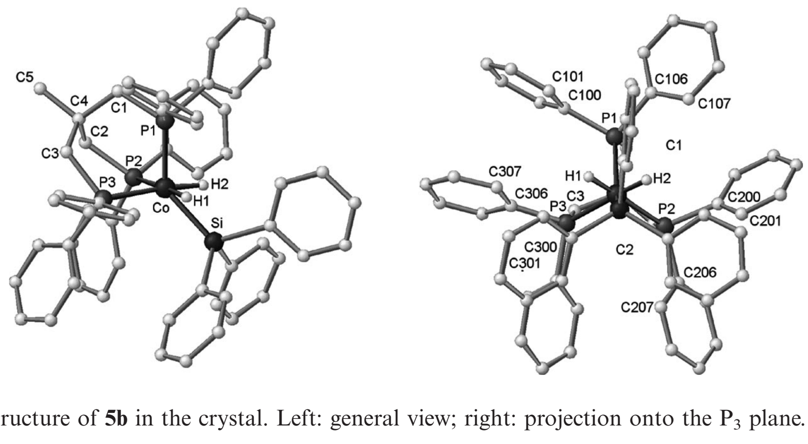


Figure 1. The molecular structure of **5b** in the crystal. Left: general view; right: projection onto the P_3 plane.

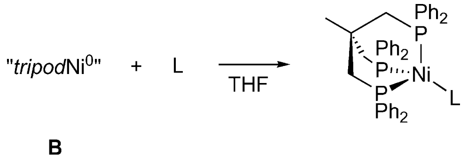
Table 1. Selected bond lengths [pm], bond angles [°] and torsion angles [°] in **4** and **5b**.

	4[a,c]	**5b**[b,c]
Co–P1	216.4(1)	217.6(1)
Co–P2	216.4(1)	217.9(1)
Co–P3	216.4(1)	218.2(1)
Co–E	246.6(1)	227.8(1)
Co–H1	–	134(3)
Co–H2	–	132(3)
E–H1	–	198(4)
E–H2	–	189(4)
H1···H2		183(6)
P1–Co–P2	93.9(1)	96.1(1)
P1–Co–P3	93.9(1)	91.6(1)
P2–Co–P3	93.9(1)	91.6(1)
P1–Co–E	139.8(1)	135.1(2)
P2–Co–E	113.3(1)	114.4(1)
P3–Co–E	112.2(1)	118.5(1)
P1–Co–H1	–	88(2)
P2–Co–H1	–	174(2)
P3–Co–H1	–	91(2)
P1–Co–H2	–	93(2)
P2–Co–H2	–	89(2)
P3–Co–H2	–	91(2)
H1–Co–E	–	60(2)
H2–Co–E	–	56(2)
H1–Co–H2	–	87(2)
τ_1[d]	30.3	24.0
τ_2[d]	30.3	10.8
τ_3[d]	30.3	13.8
f_1[e]	13.4	10.9
f_2[e]	43.3	60.6
f_3[e]	13.4	27.8
f_4[e]	43.3	37.0
f_5[e]	13.4	40.5
f_6[e]	43.3	21.0

[a] E = Sn. The labelling Scheme used for the *tripod*cobalt entity in **4** is the same as for **5a** (see Figure 1). The position of the tin atom in **4** is analogous to the position of the silicon atom in **5b**. The cobalt-bonded hydrogen atoms H1 and H2, which were found and refined isotropically in the molecular structure of **5b** in the crystal could not be located in the case of **4**. [b] E = Si. [c] The values in parentheses are standard deviations in units of the last decimals listed. [d] τ = torsion angles within the chelate cage: τ_1 = C4–C1–P1–Co, τ_2 = C4–C2–P2–Co, τ_3 = C4–C3–P3–Co. [e] The torsion angles f involving Hz are defined as follows: f_1 = Hz1–P1–C100–C101, f_2 = Hz1–P1–C106–C107, f_3 = Hz2–P2–C200–C201, f_4 = Hz2–P1–C206–C207, f_5 = Hz3–P3–C300–C301, f_6 = Hz3–P3–C306–C307; Hz–P designates a vector that is vertical to the plane formed by the three *tripod* phosphorus donor atoms and points towards the observer when, in a projection onto this plane, the vector Co–C4 points away from the observer, such that C4 lies below this plane.[9]

a species *tripod*Co at m/z = 683, this does not reveal the composition of **A** since many compounds of the type [*tripod*Co(L)$_n$]$^{n+}$ produce strong signals for [*tripod*Co]$^+$ under mass spectrometric conditions. As the solution **A** shows strongly paramagnetic properties NMR experiments are of little help.

The hope was therefore that by using nickel instead of cobalt a diamagnetic compound might possibly be obtained under otherwise analogous conditions, such that, even if the compound could not be crystallised, NMR analysis might help to clarify its constitution. When THF solutions of [(DME)NiBr$_2$] are treated with KC$_8$ in the presence of *tripod* a yellow precipitate is formed first, which by referring to literature data[10] should be [*tripod*NiBr]. This precipitate gradually dissolves again to produce an intensely yellow coloured solution, hereafter designated as solution **B**. This solution **B** apparently contains a species behaving as expected for ["*tripod*Ni^0"]: it reacts with two electron donor ligands L to form neutral nickel(0) complexes of the type [*tripod*NiL] (Scheme 4).



	6	**7**	**8**	**9**	**10**
L	PPh$_3$	AsPh$_3$	*c*HexNC	*t*BuNC	C$_2$H$_4$

Scheme 4.

Addition of PPh$_3$ and AsPh$_3$ results in the formation of the corresponding adducts **6** and **7**, respectively. The isonitriles cHexNC and *t*BuNC yield **8** and **9**. The ethylene derivative **10** is obtained by performing the reduction process of equimolar amounts of [(DME)NiBr$_2$] and *tripod* with KC$_8$ in an atmosphere of C$_2$H$_4$ instead of argon. The compounds **6**–**10** are obtained as yellow to orange coloured solids in fair yields in the range of 50–70 % in analytically pure crystalline form. Thus, they are not by-products formed by the reaction of some minor component in solution **B** but are derivatives of the main *tripod*nickel component present in this solution.

The molecular structures of **6** to **10** were elucidated by X-ray analysis. The coordination polyhedron is pseudo tetrahedral in each case. This principle is illustrated in Figure 2 with **8**, **9** and **10** as examples. Two views are given in each case, a general one demonstrating the pseudo tetrahedral geometry (left) and another one which projects the structure onto the plane of the three phosphorus atoms (right side). This last view illustrates the torsion of the *tripod* scaffolding τ and of the phenyl groups f, the numerical values of which together with some relevant distances and angles are presented in Table 2 for all compounds **6** to **10**. The Ni–P distances in **6**–**9** are 215 pm in the mean with only small deviations of individual distances from this mean value. For the ethylene derivative **10** larger Ni–P distances are observed throughout with a mean value of 218.7 pm.[11] The angles suspended by the *tripod* phosphorus atoms at nickel are definitely smaller than the ideal tetrahedral value of 109.5°. The average value amounts to 96.0° with only minor deviations from this general mean value for the individual values pertinent to each compound. Within the sets of the three values of each compound the differences observed amount to maximally 4° (see Table 2). The P–Ni–E angles – E referring to the heteroatom in the case of **6**–**9** or to the centre of the C=C bond in the case of **10** – average to 120.8°. The individual mean values of these angles referring to each of the compounds **6** to **10** are equal to this general mean value within ±1°. Nevertheless, within each set of the three P–Ni–E angles pertinent to each compound, large differences are observed (see Table 2). The maximum difference of close to 20° is observed for **9**. The diagram of the structure (see Figure 2) offers the explanation for this finding: the *t*BuNC coligand with its bulky *t*Butyl group points away from P3 bending towards the sector of P1 and P2 corresponding to a large angle P3–Ni–E. A similar orientation is observed for the cyclohexyl substituent of cHexNC in **8**, as the cyclohexyl residue now occupies the sector between P2 and P3 bending away from P1 (see Figure 2). Correspondingly, the largest P–Ni–E angle in **8** is observed for P1–Ni–E (see Table 2).

The torsion τ of the *tripod* scaffolding spreads from a minimum average value of 6.5° for **7** to a maximum of 30.0° for **10** (see Table 2). The sense of rotation was chosen for each compound such that its τ values are positive, meaning that the torsion of the scaffolding corresponds to a right-handed screw (see Figure 2, right-hand side). The orientation of the phenyl groups as described by the *f* values has

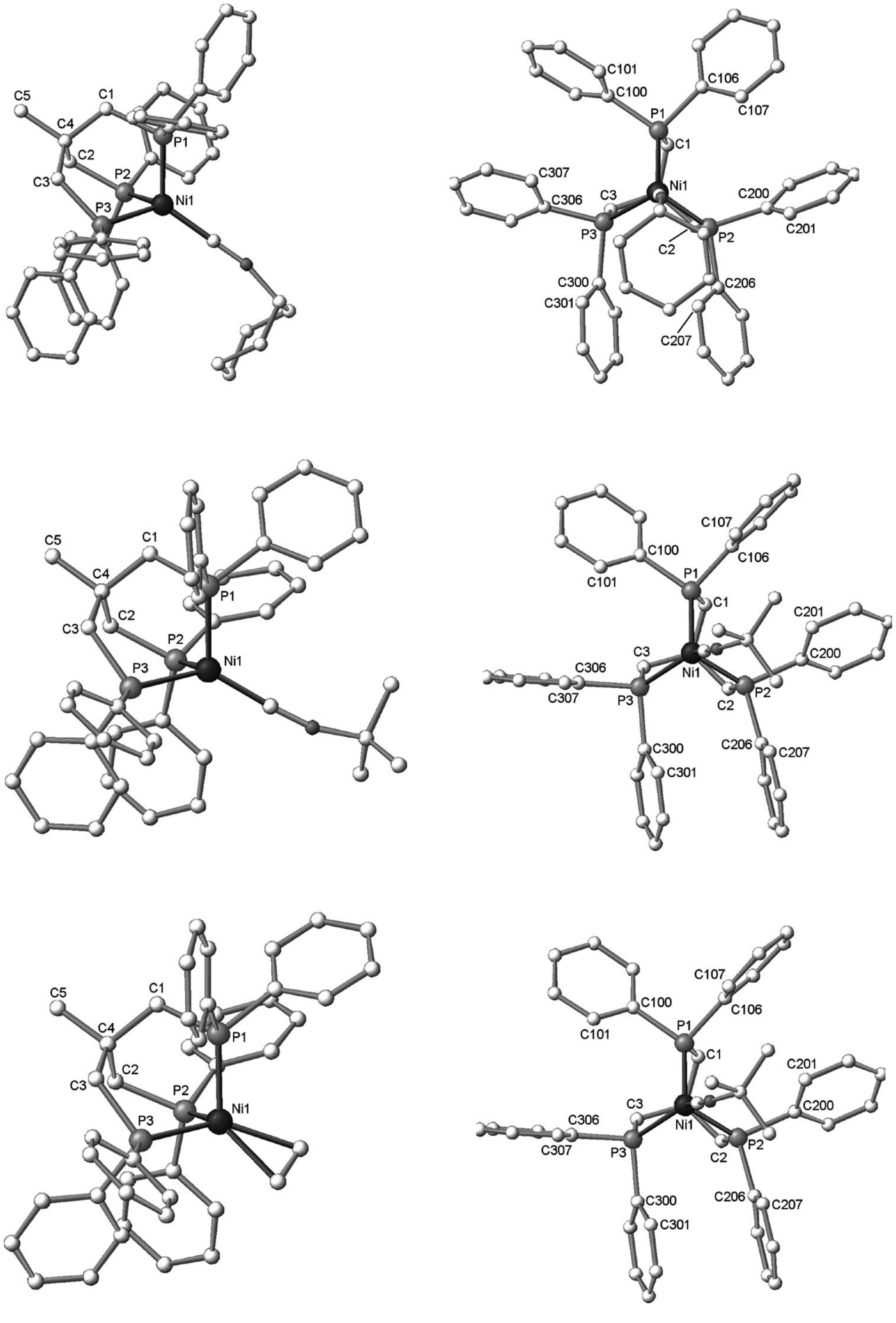


Figure 2. The molecular structures of **8** (top), **9** (middle) and **10** (bottom) in the crystal. Left: General view; right: projection onto the P_3 plane.

Table 2. Selected bond lengths [pm], bond angles [°] and torsion angles [°] for **6**–**10**.

	6[a] L = PPh_3	**7**[a] L = $AsPh_3$	**8**[a] L = cHexNC	**9**[a] L = *t*BuNC	**10**[a] L = C_2H_4
Ni–P1	215.7(2)	214.7(1)	214.4(1)	214.3(1)	219.1(1)
Ni–P2	216.1(2)	215.0(2)	215.5(1)	215.4(1)	220.2(1)
Ni–P3	215.5(2)	213.6(1)	214.8(1)	215.7(1)	216.7(1)
Ni–E	217.1(2)	228.5(1)	181.7(3)	180.6(2)	207.1(5)[e] 210.7(5)[e]
P1–Ni–P2	96.1(1)	97.3(1)	97.7(1)	96.1(1)	95.0(1)
P1–Ni–P3	95.5(1)	97.7(1)	95.4(1)	96.7(1)	95.8(1)
P2–Ni–P3	99.4(1)	97.4(1)	93.8(1)	92.3(1)	93.4(1)
P1–Ni–E[b]	121.5(1)	118.5(1)	123.9(1)	119.4(1)	120.2(2)
P2–Ni–E[b]	119.6(1)	123.0(1)	118.1(1)	112.1(1)	118.7(2)
P3–Ni–E[b]	119.4(1)	117.7(1)	121.2(1)	132.2(1)	126.5(2)
τ_1[c]	8.7	6.9	18.8	27.1	30.9
τ_2[c]	11.0	7.0	12.5	22.5	29.3
τ_3[c]	3.3	5.6	16.0	30.0	31.0
f_1[d]	45.0	42.5	20.7	50.9	59.5
f_2[d]	25.4	27.4	59.0	6.7	27.3
f_3[d]	45.1	42.2	17.5	36.7	36.1
f_4[d]	33.5	16.7	32.3	7.6	3.3
f_5[d]	50.2	50.4	21.2	15.6	37.2
f_6[d]	28.6	35.0	33.0	1.3	7.5

[a] The values in parentheses are standard deviations in units of the last decimals listed. [b] E = atom of L coordinating to nickel; in the case of **10**: centre of C=C-bond. [c] τ = torsion angles within the chelate cage: τ_1 = C4–C1–P1–Ni, τ_2 = C4–C2–P2–Ni, τ_3 = C4–C3–P3–Ni. [d] The torsion angles f involving Hz are defined as follows: f_1 = Hz1–P1–C100–C101, f_2 = Hz1–P1–C106–C107, f_3 = Hz2–P2–C200–C201, f_4 = Hz2–P1–C206–C207, f_5 = Hz3–P3–C300–C301, f_6 = Hz3–P3–C306–C307; Hz–P designates a vector that is vertical to the plane formed by the three *tripod* phosphorus donor atoms and points towards the observer when, in a projection onto this plane, the vector Co–C4 points away from the observer, such that C4 lies below this plane.[12] [e] Distance to ethylene carbon atoms.

one and the same sense for all of the six phenyl groups of all six compounds (see Table 2). The individual f values within each compound alternate systematically in so far as for each diphenylphosphane unit there is a phenyl group with a large f value while the other one has a small value (f = 0° means orientation parallel to the pseudotrigonal axis i.e. minimum visibility in the projection plane). The sequence of f values in each compound follows the pattern large–small, large–small, large–small in cyclic order (see Table 2).

The $^{31}P\{^1H\}$ NMR spectroscopic data of compounds **6** to **10** show one sharp singlet signal in the range of δ = 2.5 to δ = 7.4 for the three *tripod* phosphorus atoms of each compound, demonstrating that all three nuclei are equivalent in the time average. Observations of this kind have occasionally been made in the examination of *tripod*cobalt derivatives in the past.[5,13] As a consequence of this, it is evident that – down to the lowest achievable temperatures (183 K) – the coligands are free to rotate around their metal–ligand axis and the relative orientation of the *tripod* ligand with respect to the coligands is dynamic. ^{13}C NMR spectroscopic data are as well consistent with the formulations given. For the isocyanide derivatives **8** and **9**, the solubility of the compounds was too low and the sensitivity of the instrumentation was as well too low for allowing the observation of the quaternary carbon atoms of the coligands. ^1H NMR spectroscopic data are as expected, with the exception of the signals for the cyclohexyl moiety in **8**. At 303 K broad signals are observed for all 11 protons of the C_6H_{11} residue. Well separated from the signals generated by the CH_2 groups between δ = 1.54 and δ = 2.1, a broad signal corresponding to the proton of the CH group is observed at δ = 3.89 ppm. Upon lowering the temperature this signal broadens and vanishes in the background at 233 K. Further lowering the temperature down to 183 K causes the signal to reappear at δ = 4.15 ppm. This behaviour is typical for a dynamic equilibrium between two conformations of the cyclohexyl group, one, in which the C–H group points in an axial direction and the other one, in which its orientation is equatorial. From the coalescence temperature together with the frequency difference in the shift of the proton signal[14] the free activation energy of the process is estimated as $\Delta G^{233}_{\neq} = 47 \pm 1\,\mathrm{kJ\,mol^{-1}}$. This value is well in agreement with the values expected for ring inversions of cyclohexyl derivatives.[15]

While all the results above suggest that solution **B** contains a species reacting as would be expected for "*tripod*Ni^0" they give no hint, neither to the structure nor to the composition of such a *tripod*nickel(0) species. Referring to the rule of thumb that a nickel(0) species should have a tetrahedral environment it might well be expected that the solvent THF could play the role of the fourth ligand stabilising ["*tripod*Ni^0"] by its coordination. If no coligands were present the structure of ["*tripod*Ni^0"] should be oligomeric or polymeric in order to allow for a coordination number of four at nickel supplied by *tripod* ligands alone. Highly polymeric structures are ruled out by the observation that the compound is well soluble in THF. Fortunately enough ["*tripod*Ni^0"] is diamagnetic such that NMR spectroscopic data can be collected. To this end, in order to have a clean sample of solution **B**, the reduction of [(DME)-$NiBr_2$] by KC_8 in [D$_8$]THF was performed in an NMR tube using glove box techniques. The $^{31}P\{^1H\}$ NMR spectrum obtained with this sample is shown in Figure 3 (left).

A spectrum of this type has been repeatedly reproduced and it was shown by DOSY[16] experiments (Figure 3; right) that the observed signals most probably belong to just one chemical species since all of them are affected by diffusion to the same degree. There are four prominent multiplet signals at δ = 3.3, δ = 5.5, δ = 12.0 and δ = 28.1 with an integral ratio close to 3:1:1:1. The structure of the signal at δ = 3.3 is that of a doublet with a coupling constant of 15 Hz. Intensity and chemical shift are appropriate to the interpretation of this signal as originating from a *tripod* ligand κ^3-coordinated to nickel(0); its doublet structure and the observed coupling constant indicate the coordination of one additional phosphorus atom to this *tripod*nickel entity. This interpretation is corroborated by comparing the data with the $^{31}P\{^1H\}$ NMR spectroscopic data obtained for [*tripod*Ni(PPh_3)] (**6**): the *tripod* phosphorus atoms give rise to a signal at δ = 6.0 with a coupling constant to the phosphorus atom of the coligand PPh_3 of 15 Hz. The ^{31}P NMR

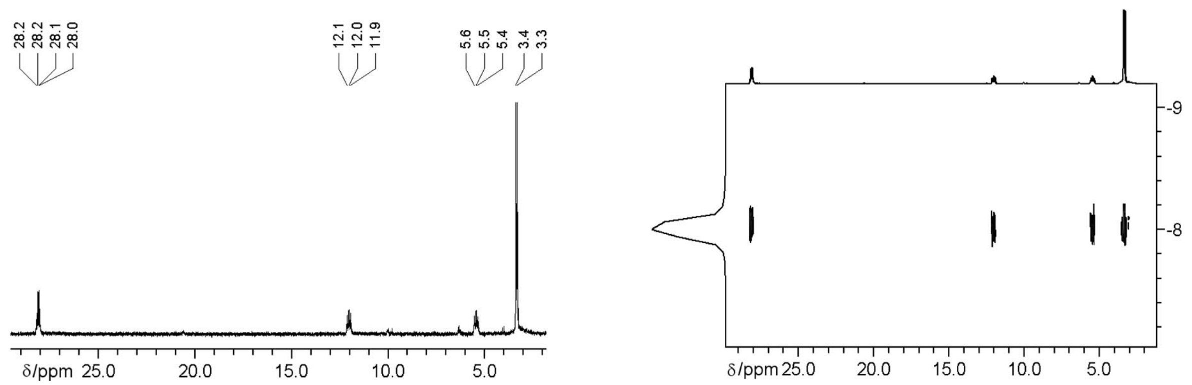
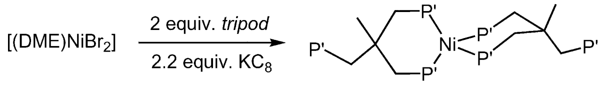


Figure 3. $^{31}P\{^1H\}$ NMR spectrum (left) and DOSY spectrum (right) of [“*tripod*Ni^0”] (**B**).

signal of the PPh_3 coligand appears at δ = 38.5 with an apparent quartet structure. In the $^{31}P\{^1H\}$ NMR spectrum of the compound analysed, the signal at δ = 28.1 likewise appears as a quartet with the same coupling constant as found for the prominent doublet at δ = 3.3 (see above). The origin of the signals at δ = 5.5 and δ = 12.0 was, however, still unclear. It was hypothesised that the signals might be due to phosphorus atoms of two pairs of PPh_2 groups, each one being part of a *tripod* ligand.

To possibly falsify this hypothesis [*tripod*$_2$Ni] (**11**) was synthesised by adding two equivalents of *tripod* to a solution of [(DME)$NiBr_2$] in THF and subsequent reduction by KC_8 (Scheme 5). This experiment was as well performed in [D$_8$]THF on an NMR scale, using glove-box techniques. The $^{31}P\{^1H\}$ NMR spectrum of [*tripod*$_2$Ni] (**11**) shows two broad signals for the coordinated phosphorus atoms in the ratio of 1:1 at δ = 6.8 and δ = 12.2 ppm. The non-coordinated arms of the two κ^2-coordinated *tripod* ligands give rise to a sharp singlet at δ = –26.7 ppm. The magnetic inequivalence of the four coordinated phosphorus atoms in two pairs is due to the axial chirality of the compound. The assignment of the signals is in full accord with the constitution of **11**, as unequivocally elucidated by X-ray analysis (Table 4).

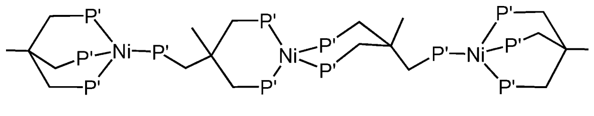


[*tripod*$_2$Ni] (**11**)

P' = PPh_2

Scheme 5.

Based on the comparison of the $^{31}P\{^1H\}$ NMR spectra of [*tripod*Ni(PPh_3)] (**6**) and [*tripod*$_2$Ni] (**11**) the $^{31}P\{^1H\}$ NMR spectroscopic data obtained for the solution of [“*tripod*Ni^0”] (**B**) allow for only one interpretation: the signals are due to a compound of the constitution [*tripod*$_4$Ni$_3$] (**12**) (Figure 4).



[*tripod*$_4$Ni$_3$] (**12**)

P' = PPh_2

Figure 4. Constitution of the reactive species [*tripod*$_4$Ni$_3$] (**12**).

This constitution with its stoichiometry of *tripod*/nickel of 4:3 is at the same time the most simple solution to the problem satisfying the coordination number of four by the *tripod* ligand having only three donor groups such that all donor groups and all metal atoms engage in coordination.

Conclusions

Treating a THF solution of [*tripod*$CoCl_2$] with KC_8 under an argon atmosphere leads to a reactive species which reacts with HER_3 (E = Si, R = Et, Ph; E = Sn, R = Bu, Ph) to produce the cobalt(III) compounds [*tripod*Co(H)$_2$-(ER_3)] (**4**, **5**). The coordination mode of these six-coordinate cobalt(III) complexes deviates strongly from octahedral coordination in that the Co–E bond bends towards the cobalt bonded hydrogen atoms. The nature and exact composition of the reactive species itself, which undergoes the oxidative addition reactions leading to **4** and **5**, is not known in this case.

In the case of nickel, by reduction of a THF solution of [(DME)$NiBr_2$] with KC_8 in the presence of *tripod* under an argon atmosphere, a reactive species is likewise obtained. It reacts with two electron donor ligands L to produce diamagnetic, pseudo tetrahedral nickel(0) complexes [*tripod*NiL] {L = PPh_3 (**6**), $AsPh_3$ (**7**), cHexNC (**8**), *t*BuNC (**9**), C_2H_4 (**10**)}. In this case the nature of the reactive species could be elucidated since, in contrast to the reactive cobalt species, the nickel(0) compound is diamagnetic. By NMR experiments its composition was unequivocally deduced to be [*tripod*$_4$Ni$_3$] (**12**). It is tempting to assume that the reactive *tripod*cobalt(0) species has an analogous constitution.

Experimental Section

General: All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or by working in a glove box. Solvents were dried with potassium (THF, DME) or CaH_2 (CH_2Cl_2, Et_2O, PE 40/60), distilled, and thoroughly degassed prior to use. Deuterated solvents were dried with potassium ([D_8]THF) or CaH_2 (CD_2Cl_2), vacuum distilled, degassed by three successive "freeze-pump-thaw"-cycles and stored in teflon valve ampoules under argon.

NMR: Bruker Avance DPX 200 at 200.120 MHz (^{1}H), 50.323 MHz [^{13}C(^{1}H)], 81.015 MHz {^{31}P{^{1}H}}; T = 303 K unless otherwise stated; chemical shifts (δ) in ppm referenced to (residual proton) peaks of CD_2Cl_2 (^{1}H: δ = 5.32; ^{13}C: δ = 53.8 ppm) and [D_8]THF (^{1}H: δ = 1.73, 3.58; ^{13}C: δ = 25.5, 67.7) as internal standards; ^{31}P chemical shifts (δ) in ppm with respect to 85% H_3PO_4 (^{31}P: δ = 0 ppm) as external standard. FAB-/HR-FAB-MS: Finnigan MAT 8400 spectrometer, xenon, matrix: 4-nitrobenzyl alcohol. LIFDI-MS: JEOL JMS-700 double-focusing magnetic sector mass spectrometer.[17] IR: BioRad Excalibur FTS 3000 spectrometer using CsI discs. UV/Vis: Perkin–Elmer Lambda 19; 0.2 cm cells (Hellma, suprasil). Cyclic Voltammetry (CV): Metrohm "Universal Meß- und Titriergefäß", Metrohm GC electrode RDE 628, platinum electrode, SCE electrode, EG&G Princeton Applied Research potentiostate Model 273, potentials in mV vs. SCE at 25 °C, sample 10^{-3} M in 0.1 M $n\mathrm{Bu}_4\mathrm{NPF}_6/\mathrm{CH}_2\mathrm{Cl}_2$. – Differential Scanning calorimetry (DSC): Mettler DSC 30, argon, 30–600 °C, heating rate: 10 K min^{-1}. Thermogravimetric Analysis (TGA): Mettler TC 15, argon, 30–600 °C, heating rate: 10 K min^{-1}. Elemental analyses: Department of Chemistry, University of Heidelberg.

Materials: 1,1,1-Tris[(diphenylphosphanyl)methyl]ethane (*tripod*) was prepared according to literature procedures.[18] All other reagents were obtained from commercial sources and used as received unless explicitly stated. Silica gel (Kieselgel z. A., 0.06–0.20 mm, J. T. Baker Chemicals B. V.) used for chromatography and kieselgur (Erg. B.6, Riedel-de Haën AG) used for filtration were degassed at 10^{-2} mbar for 48 h and saturated with argon.

General Procedure for the Synthesis of Solutions Containing A or B: KC_8 (297 mg, 2.2 mmol), prepared by heating potassium (86 mg, 2.2 mmol) with graphite (211 mg, 17.6 mmol) was added to a solution of [*tripod*$CoCl_2$] (**1**)[4] (754 mg, 1 mmol) in THF (20 mL) or [*tripod*$NiBr_2$] (840 mg, 1 mmol). [*tripod*$NiBr_2$] was prepared by treating [(DME)$NiBr_2$] (308 mg, 1 mmol) with equimolar amounts of *tripod* (624 mg, 1 mmol). The suspension resulting in each case was sonicated until the colour changed to orange brown ["*tripod*Co^0"] (**A**) or yellow brown ["*tripod*Ni^0"] (**B**), respectively. The reduction was monitored by UV/Vis spectroscopy until the spectra indicated completeness of the reaction showing a strong band at λ_{max} = 680 nm in the case of **A** and λ_{max} = 380 nm in the case of **B**. The reaction mixture was then filtered through kieselgur by means of a syringe to remove the remaining graphite.

Synthesis of [*tripod*Co(H)$_2$(SiEt$_3$)] (5a): To a THF solution containing **A**, prepared from **1**[4] (754 mg, 1 mmol) and KC_8 (297 mg, 2.2 mmol) (see above) a solution of $HSiEt_3$ (349 mg, 3 mmol) in THF (10 mL) was added. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40–60 °C) and transferred to a column containing silica gel (Ø = 3 cm, l = 5 cm), conditioning was performed with petroleum ether (boiling range 40–60 °C) via a cannula. After elution with 100 mL of petroleum ether (boiling range 40–60 °C), the product was eluted by 100 mL of diethyl ether as an orange coloured band. Having removed the solvent in vacuo, a yellow microcrystalline powder was obtained. The compound was further purified by crystallisation from diethyl ether/petroleum ether (boiling range 40–60 °C); yield 224 mg (0.28 mmol, 28%).

5a:[19] ^{1}H NMR (CD_2Cl_2): δ = –13.45 (br. s, 2 H, Co-*H*), 0.88–1.00 (m, 15 H, Si-C*H*$_2$C*H*$_3$), 1.56 (m, 3 H, *tripod*-C*H*$_3$), 2.35 (m, 6 H, *tripod*-C*H*$_2$), 6.90–7.22 (m, 30 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 41.5 (s) ppm. MS (FAB$^+$); m/z (%) [fragment]: 936 (30) [M$^+$ + matrix], 821 (70) [*tripod*Co$^+$ + matrix], 683 (20) [*tripod*Co$^+$] UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1}cm^{-1}]: 490 (sh), 520 (1250), 1034 (sh), 1310 (400).

Synthesis of [*tripod*Co(H)$_2$(SiPh$_3$)] (5b): To a THF solution containing **A**, prepared from **1**[4] (754 mg, 1 mmol) and KC_8 (297 mg, 2.2 mmol) (see above) a solution of $HSiPh_3$ (780 mg, 3 mmol) in THF (10 mL) was added. $HSiPh_3$ was purified/dried by sublimation prior to use. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40–60 °C) and transferred to a column containing silica gel (Ø = 3 cm, l = 5 cm), conditioning with petroleum ether (boiling range 40–60 °C) via a cannula. After elution by 100 mL of petroleum ether (boiling range 40–60 °C), the product was eluted by 20 mL of dichloromethane as a yellow-orange band. Having removed the solvent in vacuo, a yellow microcrystalline powder was obtained. Yield: 590 mg, 0.62 mmol, 62%. Orange crystals of **5b**, suitable for X-ray structural analysis, were obtained by layering a saturated dichloromethane solution of **5b** with diethyl ether.

5b: $C_{59}H_{56}P_3CoSi$ (944.27): calcd. C 74.99, H 5.97, P 9.83; found C 74.67, H 5.97, P 9.83. ^{1}H NMR (CD_2Cl_2): δ = –13.10 (br. s, 2 H, Co-*H*), 1.58 (s, 3 H, *tripod*-C*H*$_3$), 2.40 (s, 6 H, *tripod*-C*H*$_2$), 6.90–7.68 (m, 45 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = 39.3 (s) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 38.0 (br. s, *tripod*-*C*H$_3$), 39.5 (br. s, *tripod*-*C*H$_2$), 126.9–150.7 (aromatic *C*) ppm. MS (LIFDI); m/z (%) [fragment]: 944 (100) [M$^+$], 683 (60) [*tripod*Co$^+$]. MS (FAB$^+$); m/z (%) [fragment]: 821 (100) [*tripod*Co$^+$ + matrix],[b] 683 (60) [*tripod*Co$^+$]. IR (CsI, $\tilde{\nu}$): ν_s(Co–H) = 1928 (m), ν_{as}(Co–H) = 1916 (m) cm^{-1}. UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1}cm^{-1}]: 320 (6680), 360 (sh), 680 (90), 790 (80), 1060 (270), 1170 (sh). CV: E_p^A = –60 mV (reverse scan: –1230 mV); E_p^A = 680 mV (reverse scan: –640 mV). DSC/TGA: endothermic melting process (m.p. 260 °C) initiates exothermic decomposition, which is complete at 600 °C; exp. final weight: 11.2%; calcd. final weight [Co_2P_3]: 11.2%.

Synthesis of [*tripod*Ni(L)] (L = PPh$_3$: 6, L = AsPh$_3$: 7, L = cHexNC: 8, L = *t*BuNC: 9, L = C$_2$H$_4$: 10): To a THF solution containing **B** prepared from [*tripod*$NiBr_2$] (840 mg, 1 mmol) and KC_8 (297 mg, 2.2 mmol) (see above) a solution of L (1 mmol) in THF (10 mL) was added. After stirring overnight, the solvent was removed in vacuo. The residue was suspended in petroleum ether (boiling range 40–60 °C) and transferred to a column containing silica gel [Ø = 3 cm, l = 5 cm, conditioning with petroleum ether (boiling range 40–60 °C)] via a cannula. After elution with 100 mL of petroleum ether (boiling range 40–60 °C), the products were eluted by 20 mL of DME as yellow brown bands. Having removed the solvent in vacuo, yellow to orange coloured microcrystalline powders were obtained. Orange red crystals, suitable for X-ray structural analysis, were obtained by layering saturated DME solutions of the respective compound with petroleum ether (boiling range 40–60 °C). Yields for **6**: 410 mg, 0.43 mmol, 43%; **7**: 375 mg, 0.38 mmol, 38%; **8**: 340 mg, 0.43 mmol, 43%; **9**: 370 mg, 0.48 mmol, 48%; **10**: 400 mg, 0.56 mmol, 56%.

6: $C_{59}H_{54}P_4Ni$ (944.25): calcd. C 74.94, H 5.76, P 13.10; found C 74.79, H 5.87, P 12.82. ^{1}H NMR ([D_8]THF): δ = 1.42 (s, 3 H, *tripod*-C*H*$_3$), 2.57 (d, $^4J_{PH}$ = 2 Hz, 6 H, *tripod*-C*H*$_2$), 6.65–7.42 (m, 45 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR ([D_8]THF): δ = 6.0 (d, $^2J_{PP}$

= 15 Hz, *tripod-P*Ph$_2$), 38.5 (q, $^{2}J_{PP}$ = 15 Hz, *P*Ph$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 37.2 (br. s, *tripod*-*C*H$_3$), 43.9–43.6 (m, *tripod*-*C*H$_2$), 126.8 (s, arom. *tripod*-C_p), 127.1–127.3 (m, arom. *tripod*-C_m), 127.5 (s, PPh$_3$-C_p), 127.7 (d, $^{2}J_{CP}$ = 6 Hz, PPh$_3$-C_m), 132.8–133.3 (m, arom. *tripod*-C_o), 133.9 (d, $^{2}J_{CP}$ = 9 Hz, PPh$_3$-C_o), 141.5–142.0 (m, arom. C_q), 143.8 (m, arom. C_q) ppm. MS (HR–FAB$^+$); *m*/*z* [fragment]: 944.2552 [M$^+$, ^{58}Ni], 946.2544 [M$^+$, ^{60}Ni] (calcd. *m*/*z*: 944.2529, 946.2525) UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1} cm^{-1}]: 380 (4600), 580 (150). CV: $E_{1/2}$ = –550 mV (qrev. ox., ΔE = 170 mV), E_p^A = 600 mV, E_p^A = 1500 mV. DSC/TGA: endothermic melting process (m.p. 274 °C) initiates exothermic decomposition, which is complete at 600 °C; exp. final weight: 11.3%; calcd. final weight [Ni$_2$P$_3$]: 11.1%.

7: C$_{59}$H$_{54}$P$_3$AsNi (989.61): C 71.61, H 5.50, P 9.39; found C 71.23, H 5.75, P 9.39. ^{1}H NMR ([D$_8$]THF): δ = 1.44 (d, $^{4}J_{PH}$ = 2 Hz, 3 H, *tripod*-C*H*$_3$), 2.58 (d, $^{2}J_{PH}$ = 6 Hz, 6 H, *tripod*-C*H*$_2$), 6.65–7.47 (m, 45 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 7.4 (s) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 36.9 (q, $^{2}J_{CP}$ = 7 Hz, CH$_3$-C$_q$), 37.5 (q, $^{3}J_{CP}$ = 10 Hz, *tripod*-*C*H$_3$), 42.6–43.0 (m, *tripod*-*C*H$_2$), 126.4 (s, arom. *tripod*-C_p), 126.7–126.8 (m, arom. *tripod*-C_m), 127.4 (s, AsPh$_3$-C_p), 127.6 (s, AsPh$_3$-C_m), 132.3–132.4 (m, arom. *tripod*-C_o), 133.5 (s, AsPh$_3$-C_o), 143.0–143.5 (m, arom. C_q) ppm. MS (FAB$^+$); *m*/*z* (%) [fragment]: 988 (1) [M$^+$], 820 (5) [*tripod*Ni$^+$ + matrix], 682 (20) [*tripod*Ni$^+$]. UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1} cm^{-1}]: 380 (21500). CV: $E_{1/2}$ = –260 mV (qrev. ox., ΔE = 100 mV), E_p^C = –1600 mV (reverse scan –500 mV), E_p^A = 1690 mV. DSC/TGA: endothermic melting process (m.p. 256 °C) initiates exothermic decomposition, which is complete at 600 °C; exp. final weight: 15.9%; calcd. final weight [Ni$_2$P$_3$]: 21.4%.

8: C$_{48}$H$_{50}$P$_3$NNi (792.55): C 72.74, H 6.36, P 11.72, N 1.77; found C 72.51, H 6.37, P 11.88, N 1.80. ^{1}H NMR ([D$_8$]THF, 303 K): δ = 1.40 (d, $^{4}J_{PH}$ = 2 Hz, 3 H, *tripod*-C*H*$_3$), 1.54 (br. s, 4 H, cHex-C*H*$_2$), 2.00 (br. s, 6 H, cHex-C*H*$_2$), 2.18 (d, $^{2}J_{PH}$ = 5 Hz, 6 H, *tripod*-C*H*$_2$), 3.89 (br. s, 1 H, cHex-C*H*), 6.84–7.40 (m, 30 H, arom. *H*) ppm. ^{1}H NMR ([D$_8$]THF, 183 K): δ = 1.34 (m, 8 H, *tripod*-C*H*$_3$, cHex-CH$_2$), 2.11–2.43 (m, 10 H, *tripod*-C*H*$_2$, cHex-C*H*$_2$), 3.14 (br. s, 1 H, cHex-C*H*$_2$), 4.15 (br. s, 1 H, cHex-C*H*), 6.84–7.40 (m, 30 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 7.3 (s) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 23.2 (s, cHex-*C*H$_2$), 26.1 (s, cHex-*C*H$_2$), 34.2 (s, cHex-*C*H$_2$), 37.1–37.8 (m, *tripod*-*C*H$_3$, *tripod*-*C*H$_2$), 53.6 (s, cHex-*C*H), 126.9 (s, arom. *tripod*-C_p), 127.0–127.3 (m, arom. *tripod*-C_m), 131.8–132.1 (m, arom. *tripod*-C_o), 142.9–143.0 (m, arom. C_q) ppm. ^{13}C DEPT NMR ([D$_8$]THF): δ = 23.2 (s, cHex-*C*H$_2$), 26.1 (s, cHex-*C*H$_2$), 34.2 (s, cHex-*C*H$_2$), 37.1 (m, *tripod*-*C*H$_2$), 37.2–37.8 (m, *tripod*-*C*H$_3$), 53.6 (s, cHex-*C*H), 128.9 (s, arom. *tripod*-C_p), 127.0–127.3 (m, arom. *tripod*-C_m), 131.8–132.1 (m, arom. *tripod*-C_o) ppm. MS (HR–FAB$^+$); *m*/*z* [fragment]: 791.2565 [M$^+$, ^{58}Ni], 793.2508 [M$^+$, ^{60}Ni] (calcd. *m*/*z*: 791.2510, 793.2495). UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1} cm^{-1}]: 360 (4900). CV: $E_{1/2}$ = –530 mV (rev. ox., ΔE = 200 mV), E_p^A = 760 mV (reverse scan: –220 mV). DSC/TGA: endothermic melting process (m.p. 230 °C) initiates exothermic decomposition, which is complete at 600 °C; exp. final weight: 6.8%; calcd. final weight [Ni$_2$P$_3$]: 13.3%.

9: C$_{46}$H$_{48}$P$_3$NNi (766.51): C 72.08, H 6.31, P 12.12, N 1.83; found C 71.99, H 6.34, P 12.22, N 1.92. ^{1}H NMR ([D$_8$]THF): δ = 1.40 (br. s, 3 H, *tripod*-C*H*$_3$), 1.63 (s, 9 H, *t*Bu-C*H*$_3$), 2.18 (d, $^{2}J_{PH}$ = 5 Hz, 6 H, *tripod*-C*H*$_2$), 6.85–7.41 (m, 30 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 7.3 (s) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 31.6 (s, *t*Bu-*C*H$_3$), 36.7–37.3 (m, *tripod*-*C*H$_2$), 37.6–38.0 (m, *tripod*-*C*H$_3$), 127.0 (s, arom. *tripod*-C_p), 127.1–127.3 (m, arom. *tripod*-C_m), 131.7–132.3 (m, arom. *tripod*-C_o), 142.4–143.2 (m, arom. C_q) ppm. MS (HR–FAB$^+$); *m*/*z* [fragment]: 765.2299 [M$^+$, ^{58}Ni], 767.2333 [M$^+$, ^{60}Ni] (calcd. *m*/*z*: 765.2353, 767.2336). UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1} cm^{-1}]: 360 (6700). CV: $E_{1/2}$ = –540 mV (rev. ox., ΔE = 120 mV), E_p^A = 1130 mV, E_p^A = 1740 mV, E_p^C = –2110 mV (reverse scan: –50 mV). DSC/TGA: endothermic melting process (m.p. 204 °C) initiates exothermic decomposition, which is complete at 600 °C; exp. final weight: 19.1%; calcd. final weight [Ni$_2$P$_3$]: 13.8%.

10: C$_{43}$H$_{43}$P$_3$Ni (711.43): C 72.60, H 6.09, P 13.06; found C 72.05, H 5.98, P 13.12. ^{1}H NMR ([D$_8$]THF): δ = 1.49 (br. s, 3 H, *tripod*-C*H*$_3$), 2.32 (br. s, 6 H, *tripod*-C*H*$_2$), 3.25 (s, 4 H, C$_2$*H*$_4$), 6.86–7.07 (m, 30 H, arom. *H*) ppm. ^{31}P{^{1}H} NMR ([D$_8$]THF): δ = 2.5 (s) ppm. ^{13}C{^{1}H} NMR ([D$_8$]THF): δ = 36.5–36.9 (q, $^{2}J_{CP}$ = 7 Hz, CH$_3$-C_q), 37.0–37.6 (q, $^{3}J_{CP}$ = 10 Hz, *tripod*-*C*H$_3$), 37.8–38.2 (m, *tripod*-*C*H$_2$), 43.1 (m, *C*$_2$H$_4$), 127.1 (s, arom. *tripod*-C_p), 127.5–127.7 (m, arom. *tripod*-C_m), 131.7–132.0 (m, arom. *tripod*-C_o), 142.3–143.1 (m, arom. C_q) ppm. ^{13}C DEPT NMR ([D$_8$]THF): δ = 37.4–38.0 (m, *tripod*-*C*H$_3$), 38.2–38.6 (m, *tripod*-*C*H$_2$), 43.4 (br. s, *C*$_2$H$_4$), 127.1 (s, arom. *tripod*-C_p), 127.4–127.6 (m, arom. *tripod*-C_m), 131.6–131.9 (m, arom. *tripod*-C_o) ppm. MS (LIFDI); *m*/*z* [fragment]: 710 [M$^+$] (100). UV/Vis (THF), λ_{max} [nm] (ε) [M^{-1} cm^{-1}]: 340 (5660), 430 (3460). CV: $E_{1/2}$ = –290 mV (rev. ox., ΔE = 120 mV), E_p^A = 1100 mV, E_p^A = 1520 mV, E_p^C = –1010 (reverse scan: –610 mV). DSC/TGA: endothermic melting process (m.p. 223 °C) initiates exothermic decomposition, which is complete at 600 °C; exp. final weight: 21.0%; calcd. final weight [Ni$_2$P$_3$]: 14.8%.

Synthesis of [*tripod*$_2$Ni] (11): [(DME)NiBr$_2$] (31 mg, 0.1 mmol) and *tripod* (125 mg, 0.2 mmol) are dissolved in [D$_8$]THF (2 mL). This solution was treated with KC$_8$ (30 mg, 0.22 mmol) and sonicated. Within 10 min a yellow solid precipitates which dissolves again whereby a yellow brownish solution is obtained. The reaction mixture was then filtered through kieselgur by means of a syringe to remove the remaining graphite. The resulting solution was used for NMR experiments. Yellow crystals, suitable for X-ray structural analysis, were obtained after concentrating and storing this solu-

Table 3. Crystal data for **4** and **5b**.

Compound	**4**	**5b**
Empirical formula	C$_{53}$H$_{68}$P$_3$CoSn	C$_{59}$H$_{56}$P$_3$CoSi
Molecular mass [g]	975.69	944.97
Crystal size [mm]	0.15 × 0.05 × 0.05	0.50 × 0.25 × 0.25
Crystal system	cubic	orthorhombic
Space group (No.)	$I\bar{4}3d$ (220)	$Pna2_1$ (3 3)
a [pm]	2688.1(3)	1857.1(4)
b [pm]	2688.1(3)	1349.1(3)
c [pm]	2688.1(3)	1899.7(4)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [10^6 pm^3]	19425	4760
Z	16	4
$d_{calcd.}$ [g cm^{-3}]	1.294	1.319
T [K]	200	200
Scan range	3.7° ≤ 2θ ≤ 50.1°	3.7° ≤ 2θ ≤ 55.0°
Method	ω scan, $\Delta\omega$ = 1°	ω scan, $\Delta\omega$ = 1°
Scan speed [s frame^{-1}]	60	8
No. of reflections measured	32884	10942
No. of unique reflections	2874	10522
No. reflections observed	2288	9371
Observation criterion	$I \geq 2\sigma$	$I \geq 2\sigma$
No. of parameters refined	196	585
Resididual electron density [10^{-6} e pm^{-3}]	0.54	0.26
R_1/R_w (%) (F^2 refinement)	4.9/13.1	3.6/7.9

Table 4. Crystal data for **6**, **7**, **8**, **9**, **10** and **11**.

Compound	**6**	**7**	**8**	**9**	**10**	**11**
Empirical formula	$C_{59}H_{54}P_4Ni{\cdot}DME$	$C_{59}H_{54}P_3AsNi$	$C_{48}H_{50}P_3NNi$	$C_{46}H_{48}P_3NNi$	$C_{43}H_{43}P_3Ni$	$C_{82}H_{78}P_6Ni{\cdot}2THF$
Molecular mass	1035.73	989.61	792.55	766.51	711.43	1452.27
Crystal size [mm]	0.25 × 0.25 × 0.20	0.50 × 0.50 × 0.30	0.50 × 0.50 × 0.25	0.30 × 0.30 × 0.20	0.25 × 0.20 × 0.20	0.22 × 0.13 × 0.05
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group (No.)	$P\bar{1}$(2)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/n$ (14)
Lattice constants:						
a [pm]	1187.4(2)	2647.9(5)	1299.0(3)	1944.6(4)	1021.8(2)	1520.3(3)
b [pm]	1591.7(3)	1827.2(4)	1422.6(3)	1242.2(3)	2019.6(4)	2178.8(4)
c [pm]	1661.0(3)	2172.1(4)	2144.1(4)	1728.3(4)	1738.0(4)	2539.5(5)
α [°]	75.15(3)	90	90	90	90	90
β [°]	82.31(3)	113.15(3)	91.59(3)	108.00(3)	97.72(3)	99.26(3)
γ [°]	74.95(3)	90	90	90	90	90
V [10^6 pm^3]	2923	9663	3961	3971	3554	8302
Z	2	8	4	4	4	4
$d_{calcd.}$ [g cm^{-3}]	1.177	1.360	1.329	1.282	1.330	1.162
T [K]	200	200	200	200	200	100
Scan range	$2.5° \leq 2\theta \leq 59.8°$	$2.8° \leq 2\theta \leq 55.1°$	$3.4° \leq 2\theta \leq 55.0°$	$4.1° \leq 2\theta \leq 55.0°$	$3.1° \leq 2\theta \leq 55.0°$	$2.5° \leq 2\theta \leq 46.5°$
Method	ω scan, $\Delta\omega = 1°$	ω scan, $\Delta\omega = 1°$	ω scan, $\Delta\omega = 1°$	ω scan, $\Delta\omega = 1°$	ω scan, $\Delta\omega = 1°$	ω scan, $\Delta\omega = 1°$
Scan speed [s frame^{-1}]	10	10	10	10	30	15
No. of reflections measured	19635	40626	16613	16856	10098	12303
No. of unique reflections	13212	21984	9054	9037	7966	11922
No. reflections observed	7943	11966	6043	6542	4451	5484
Observation criterion	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$
No. of parameters refined	662	1163	526	468	429	745
Resididual electron density [10^{-6} e pm^{-3}]	1.63	0.87	0.39	0.47	0.83	1.83
R_1/R_w [%]F^2 refinement	8.9/30.0	6.0/16.1	4.7/10.5	4.2/10.2	7.6/21.5	13.8/38.7

tion at –10 °C. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = –26.7 (s, 2 P), 6.8 (br. s, 2 P), 12.2 (br. s, 2 P) ppm.

Synthesis of [*tripod*$_4$Ni$_3$] (12): Synthesis follows the procedure described for the synthesis of solutions containing **B**. [(DME)NiBr$_2$] (31 mg, 0.1 mmol) and *tripod* (62 mg, 0.1 mmol) are dissolved in [D$_8$]THF (2 mL). This solution was treated with KC$_8$ (30 mg, 0.22 mmol) and sonicated. Within 10 min a yellow solid precipitates which dissolves again whereby a yellow brownish solution is obtained. The reaction mixture was then filtered through kieselgur by means of a syringe to remove the remaining graphite. The resulting solution was used for NMR experiments. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 3.3 (d, $^2J_{PP}$ = 15 Hz, 3 P), 5.5 (m, 1 P), 12.0 (m, 1 P), 28.1 (q, $^2J_{PP}$ = 15 Hz, 1 P) ppm. For more detailed NMR spectroscopic data see Figure 3.

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. Measurements were made on a Nonius-Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo-K_α radiation. The temperature was set to 200 K. The data collected were processed using the standard Nonius software.[20] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[21,22] Graphical handling of the structural data during solution and refinement was performed with XPMA.[23] Structural representations were generated using Winray 32.[24] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations. Data relating to the structure determinations are compiled in Tables 3 and 4.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-657981 (for **4**), -657982 (for **9**), -657983 (for **8**), -657984 (for **7**), -657985 (for **6**), -657986 (for **11**), -657987 (for **5b**) and -657988 (for **10**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K., Fax: +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk.

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[6] The molecular structure of **4** in the crystal was solved in space group $I\bar{4}3d$. While it is accurately determined (see Tables 1 and 3) there is an appearing disorder of the orientation of the $SnBu_3$ group over three positions since the cobalt atom occupies a position at a crystallographic trigonal axis. This appearing disorder problem – which does not affect the accuracy of the determination of the molecular structure to a great extent – might be due to a twin problem or to an overstructure phenomenon. No attempt has been made to untangle this problem.

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[11] Compound **10** crystallises in the space group $P2_1/n$. The solution of the molecular structure in the crystal was straightforward and the agreement factors are satisfactory (see Table 4). A peculiarity is, however, that the ethylene C–C distance was determined as only 116.4(8) pm. Inspection of the size and orientation of the thermal ellipsoids of the ethylene carbon atoms gives a clue to a rational interpretation of this seemingly short C–C distance: the thermal ellipsoids are oriented such that their longest axes almost lie in the C–Co–C plane. This could mean that there are two positions available for the ethylene entity, both of them in the C–Co–C plane, but slightly displaced from the observed position on either side. Further refinement using an appropriate model of disorder, for instance starting with a physically realistic contrained C–C distance, was not considered necessary.

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